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Final Report

Electronic Structure Calculations at Macroscopic Scales

Principal Investigator:
Vikram Gavini
Department of Mechanical Engineering
University of Michigan, Ann Arbor

Program Manager:
Fariba Fahroo
Mathematics Information and Life Sciences Directorate
Air Force Office of Scientific Research

Abstract

This report summarizes the research objectives achieved in this project during the period 03-01-2009 to 12-31-2011. Computational techniques have been developed that enable electronic structure calculations at macroscopic scales by seamless bridging of the quantum length-scale with continuum. The various components of the developed multi-scale scheme include (i) real-space formulation of density-functional theory (DFT); (ii) finite-element discretization; (iii) an adaptive coarse-graining through quasi-continuum reduction. The formulation has been developed for orbital-free DFT with non-local kinetic energy functionals. Studies on the energetics of defects in materials using the developed techniques have provided many new insights into the behavior of defects, and the complex nature of the interacting length-scales that influence their behavior. An extension of this formulation to Kohn-Sham DFT was attempted, and as part of this effort an efficient real-space formulation of Kohn-Sham DFT was developed. Studies show that the developed formulation compares favorably with existing conventional DFT implementations, enables consideration of complex geometries and boundary conditions, and exhibits good scalability on parallel computing architectures.

Summary of Research Objectives Achieved

In this project we have conducted a program of research to develop computational techniques that seamlessly bridge the quantum length-scale with the continuum and enable an accurate electronic structure study of defective crystals. The techniques have been developed for orbital-free DFT (Wang & Teter, 1992; Wang et al., 1998, 1999), which is an approximation to the Kohn-Sham density functional theory where the kinetic energy functionals are modeled and is applicable to materials systems whose electronic structure is close to a free electron gas. Further, in order to extend these techniques to Kohn-Sham density functional theory, we have developed a real-space formulation of Kohn-Sham density functional theory (Suryanarayana et al., 2010; Motamarri et al., 2012), which is the basis for the coarse-graining techniques based on quasi-continuum reduction (Gavini et al., 2007; Radhakrishnan & Gavini, 2010). A comprehensive summary of the important research objectives achieved in this project is presented below with references to the published articles.

1 Development of quasi-continuum reduction of orbital-free DFT with non-local kinetic energy functionals and Mathematical Analysis:

We have accomplished the quasi-continuum reduction of orbital-free DFT with non-local kinetic energy functionals (Radhakrishnan & Gavini, 2010), which has enabled electronic structure calculations using orbital-free DFT without cell-size restrictions and has enabled an accurate electronic structure study of defects within the framework of orbital-free DFT. One of the significant challenges in the development of the formulation was the incorporation of non-local kinetic energy functionals, density-independent (DI) and density-dependent (DD) functionals, into the quasi-continuum reduction which is based on a local variational formulation. These non-local kernel energies constitute an important part of the orbital-free kinetic energy functional, which are necessary to satisfy the Lindhard response function—a known limiting behavior of uniform electron gas. The Wang-Govind-Carter (WGC) kinetic energy functional (Wang et al., 1999), which falls into the family of DD kernel energies, has been shown to be a transferable kinetic energy functional which predicts a wide range of bulk and defect properties in Aluminum. To address this challenge, we developed a local variational formulation of these extended kinetic energy functionals through a system of coupled Helmholtz equations (Radhakrishnan & Gavini, 2010). The resulting local real-space saddle-point formulation was discretized using a finite-element basis, and the computed ground-state properties were in excellent agreement with the Fourier space calculations. The quasi-continuum reduction of orbital-free DFT including the DI and DD kinetic energy functionals was subsequently implemented taking advantage of the adaptive coarse-graining capability of the finite-element basis. We subsequently conducted a cell-size study on the formation energies of vacancies by considering cell-sizes up to a million atoms. These studies have revealed larger cell-size effects in the computed energetics than previously reported, and have demonstrated that long-ranged electronic and elastic fields play an important role in governing the energetics of defects (cf. figures 1 and 2).
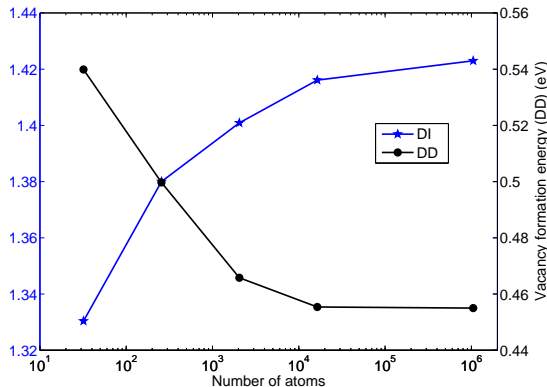

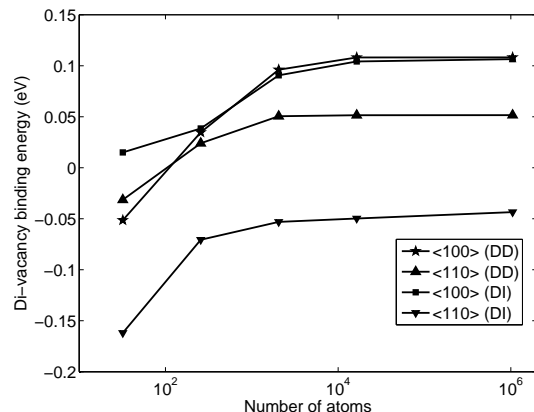Figure 1: Effect of cell-size on mono-vacancy formation energy.

Figure 2: Effect of cell-size on di-vacancy binding energy.

As part of this work we also conducted a mathematical analysis of the quasi-continuum reduction technique (Gavini & Liu, 2011). In particular, by perturbation method and multiple scale analysis, we provided a formal justification for the validity of numerical coarse-graining

of various fields in the quasi-continuum reduction of orbital-free DFT by taking the homogenization limit. Further, we derived the homogenized equations that govern the behavior of electronic fields in regions of smooth deformations. Using Fourier analysis, we determined the far-field solutions for the electronic and elastic fields in the presence of local defects, and subsequently estimate cell-size effects in computed defect energies. Our studies have indicated that even for weak defects like vacancies, the perturbations in electronic fields in the presence of the defects have non-vanishing contributions to the energy up to cell-size of the order of 1000 atoms which is consistent with the results from our numerical investigations.

2   Real-space formulation of Kohn-Sham density functional theory and Mathematical analysis:

The validity of orbital-free DFT is restricted only to material systems whose electronic structure is close to a free-electron gas—simple metals and Aluminum. In order to over come this limitation we have developed a local real-space variational formulation of Kohn-Sham DFT (Suryanarayana et al., 2010). In particular, the extended electrostatic interactions are reformulated as a local variational problem by solving the Poisson equation, and the computation of ground-state properties in Kohn-Sham DFT reduces to a local saddle-point problem in the vector containing the single-electron wave-functions and the electrostatic potential. We note that this variational formulation is equivalent to solving an eigen-value problem, with the eigenfunctions representing the single-electron wave-functions, in a self-consistent iteration representing a fixed point iteration of the Kohn-Sham map. The numerical discretization of the formulation has been implemented using a finite-element basis constructed from a finite-element triangulation of the domain with linear tetrahedral elements. Both the non-linear variational formulation and the self-consistent fixed point iteration approach solving the eigenvalue problem have been numerically implemented and benchmark studies have been conducted. An important outcome of the present study was the excellent scalability of the discrete formulation on parallel computing architectures afforded by the finite-element basis as well as the ability to handle both pseudopotential and all-electron calculations with complex boundary conditions. However, this study also demonstrated the computational inefficiency of linear finite-element basis functions in electronic structure calculations performed using Kohn-Sham DFT. It was seen that about 100,000 linear FE basis functions per atom were required to achieve chemical accuracy, which is significantly larger than other basis functions like plane-wave basis and Gaussian basis functions. In order to address this bottleneck, we have developed the framework for higher-order finite-element discretization that is discussed subsequently.

As part of this work we also conducted the mathematical analysis of the variational formulation of Kohn-Sham DFT (Suryanarayana et al., 2010). In particular, using the direct method in the calculus of variations, we proved the existence of solutions of variational problem. A key idea used in this proof includes Sobolev embeddings to prove the lower semi-continuity in the weak topology. Further, we show the $\Gamma-$convergence of the finite-element discretization, which is a variational notion of convergence for non-linear functionals. As a further part of this study we also prove the $\Gamma-$convergence of the finite-element discretization with numerical quadratures of sufficient accuracy. A key idea in this proof involves the use inverse inequalities to show the equi-coercivity of the sequence of functionals in the weak topology.

3 Computational efficiency afforded by higher order finite-element discretization in electronic structure calculations:

Our studies indicated that linear FE basis functions are computationally inefficient in electronic structure calculations which require chemical accuracy. To this end we explored the computational efficiency afforded by higher-order finite-element discretizations. In particular, we developed a framework for higher order finite-element discretizations which include quadratic tetrahedral FE basis functions, and hexahedral node-based Lagrange basis functions up to 10th order which includes spectral elements. We conducted systematic studies to assess the computational efficiency afforded by higher-order FE discretizations for both orbital-free DFT (Motamarri et al., 2011) and Kohn-Sham DFT (Motamarri et al., 2012). Our benchmark numerical studies demonstrated optimal rates of convergence for these discretization based on linear finite-element analysis although the present problem is non-linear. Further, more interestingly, the optimal rates of convergence were also observed for all-electron calculations, which represents a system with Coulomb singularity in the electrostatic potential. To the best of our knowledge there is no mathematical theory which guarantees the optimal rates of convergence in all-electron calculations, and the present studies provide the first numerical evidence for optimal convergence. While higher-order discertizations are more accurate and require lesser number of basis functions to achieve chemical accuracy in comparison to a lower-order discretization, the per basis computational cost is also higher for higher-order discretizations. Thus, in order to assess the computational efficiency of higher order finite-element discretizations we conducted a study to compare the CPU times required to compute the electronic structure of benchmark problems using various orders of finite-element basis functions. Our studies indicate that a 4th order FE basis function provides a staggering 100-1000 fold computational savings in comparison to a linear FE basis function. This clearly demonstrates the computational efficiency afforded by higher order discretizations in electronic structure calculations. Further, we observed that spectral FE basis functions improve the conditioning of the system and result in a faster convergence of the iterative algorithms.
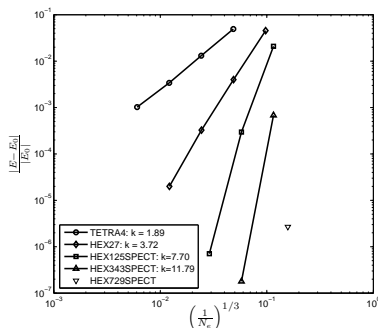

Figure 3: Convergence of error in ground-state energy of a 35-atom Barium cluster for various orders of finite-elements.
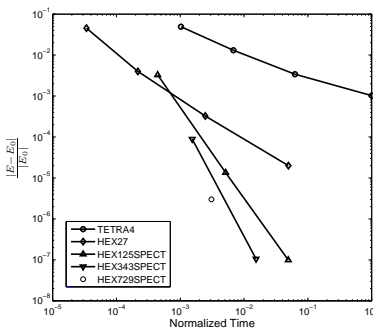
Figure 4: Relative performance of various orders of finite-elements measured in terms of computational time.
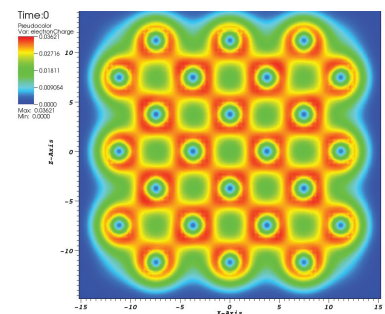
Figure 5: Electron-density contours of an Aluminum cluster with 172 atoms.

The spectral FE basis functions have a special role in Kohn-Sham DFT calculations. The

discrete eigenvalue problem while using spectral FE basis functions reduces to a standard eigenvalue problem for which efficient numerical techniques have been previously developed. In particular, in the present work, we took advantage of the Chebyschev acceleration technique to solve for the subspace spanned by the single-electron wave-functions. Upon computing the eigenspace, we project the Hamiltonian into this eigenspace to solve a smaller eigenvalue problem in the subspace, which is numerically more efficient than solving the eigenvalue problem in the original space. We conducted benchmark studies to compare the performance of our implementation with existing softwares like ABINIT and Gaussian. The proposed approach to the solution of the Kohn-Sham DFT problem with higher-order FE basis functions is comparing favorably with existing highly optimized commercial codes (Motamarri et al., 2012). Moreover, we note that the finite-element discretization offers many other advantages, which include the ability to handle complex geometries and boundary conditions, good scalability on parallel computing architectures, and the ability to handle both pseudopotential and all-electron calculations.

4 Tensor-structured techniques for electronic structure calculations:
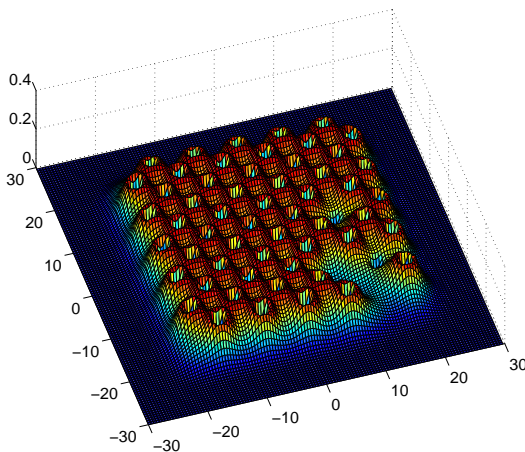

Figure 6: Electron density contours (computed from OFDFT) of a cluster containing 666 Aluminum atoms with random replacement of 20 Aluminium atoms by 10 Lithium atoms and 10 vacancies. Contours at sectional plane $y = -8$.
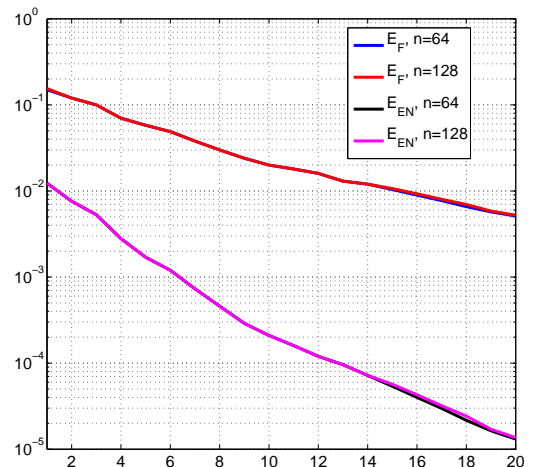
Figure 7: The convergence of the approximation error with respect to the Tucker tensor rank in the Frobenius and energy norms for varying univariate grid-size $n = 64, 128$.

In the course of this project, a new research direction emerged. Low-rank tensor representations of the multi-dimensional data based on the canonical and Tucker models have been in use in signal processing and computer science (De Lathauwer et al., 2000a,b; Kolda & Bader, 2007). Recent developments in tensor-structured methods also dramatically reduce the complexity of the numerical evaluation of the multivariate functions and operators in $\mathbb{R}^d$, $d \geq 3$. Algebraically separable tensor approaches have recently been applied to electronic structure calculations in the context of Hartree-Fock equation (Khoromskij et al., 2011; Khoromskaia et al., 2011). We conducted a study to investigate dependence of the rank

of the Tucker approximation of the electronic structure of systems with varying sizes. To this end, we computed the electronic structure of varying size of Aluminum clusters which include $1 \times 1 \times 1$ FCC unit cells to $5 \times 5 \times 5$ FCC unit cells using orbital-free DFT. The Tucker representation of this data was subsequently computed and analyzed in collaboration with Dr. Blesgen and Dr. Khoromskaia at the Max-Planck Institute for Mathematical Sciences. The analysis showed that a rank of less than 10 was sufficient to approximate the electronic structure of the various systems with varying sizes, and the rank was independent of the number of atoms in the system for the systems considered (Blesgen et al., 2011). As a more stringent test, we replaced at random 20 Aluminum atoms in a non-periodic $5 \times 5 \times 5$ FCC Aluminum cluster with 666atms with with 10 vacancies and 10 Lithium atoms. Our studies show that a Tucker rank of 20 was sufficient to approximate the electron-density of this materials system, suggesting that tensor-structured techniques based on Tucker representation may be efficient representations of electronic structures. These studies open the possibility of computing both the orbital-free DFT problem and Kohn-Sham DFT problem using tensor-structured techniques, and the development of these algorithms is currently being pursued.

5   Application studies:

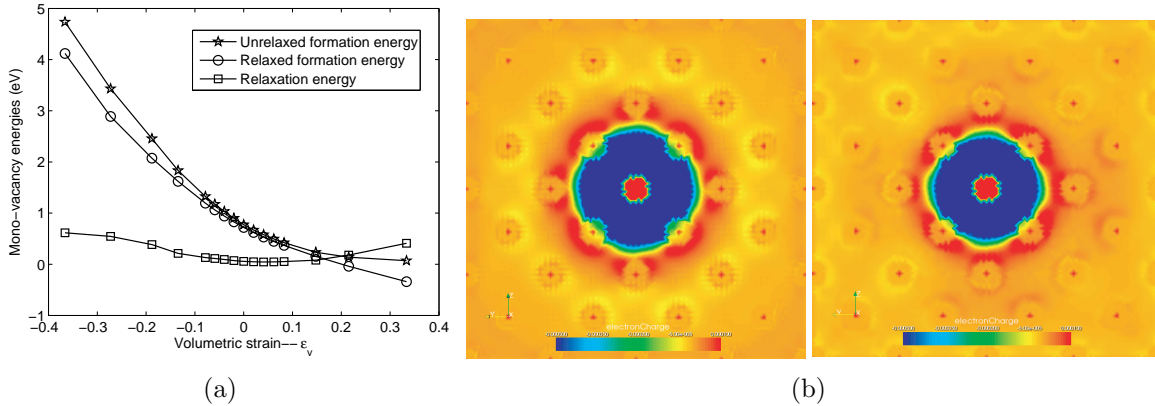(a)   (b)

Figure 8: (a) Dependence of vacancy formation energy on macroscopic deformations computed using quasi-continuum orbital-free DFT. (b) Contours of perturbation in electron-density in the presence of a vacancy; left: no imposed deformation; right: 0.33 volumetric strain.

We used the quasi-continuum reduction of orbital-free DFT to investigate if the defect-core governed by quantum-mechanical interactions plays a crucial role in the energetics of defects by studying vacancies in Aluminum. We find that vacancy core-energy is significantly influenced by the state of deformation at the vacancy-core, especially volumetric strains (Gavini, 2009). Insights from the core electronic structure and computed displacement fields show that this dependence on volumetric strains is closely related to the changing nature of the core-structure under volumetric deformations (cf. figure 8). These results are in sharp contrast to mechanics descriptions based on elastic interactions that often consider defect core-energies as an inconsequential constant. Calculations suggest that the variation in core-energies with changing macroscopic deformations is quantitatively more significant

than the corresponding variation in relaxation energies associated with elastic fields. Upon studying the influence of various macroscopic deformations, which include volumetric, uni-axial, biaxial and shear deformations, on the formation energies of vacancies, we show that volumetric deformations play a dominant role in governing the energetics of these defects. Further, by plotting formation energies of vacancies and di-vacancies against the volumetric strain corresponding to any macroscopic deformation, we find that all variations in the formation energies collapse on to a universal curve. This suggests a universal role of volumetric strains in the energetics of vacancies. Implications of these results in the context of dynamic failure in metals due to spalling are analyzed.

6 Publications supported by AFOSR

1 Gavini, V., Role of the defect core in energetics of vacancies, *Proc. Roy. Soc. A* **465**, 3239-3266 (2009).

2 Suryanarayana, P., Gavini, V., Blesgen, T., Bhattacharya, K., Ortiz, M., Non-periodic finite-element formulation of KohnSham density functional theory, *J. Mech. Phys. Solids* **58**, 256-280 (2010).

3 Radhakrishnan, B., Gavini, V., Effect of cell size on the energetics of vacancies in aluminum studied via orbital-free density functional theory, *Phys. Rev. B* **82**, 094117 (2010).

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6 Blesgen, T., Gavini, V., Khoromskaia, V., Approximation of the Electron Density of Aluminium Clusters in Tensor-Product Format, *J. Comp. Phys.* **231** 2551-2564 (2012).

7 Radhakrishnan, B. G., Gavini, V., Electronic structure calculations at macroscopic scales using orbital-free DFT, In Wang, Y.A., Wesolowski, T. (Ed.) Recent Advances in Orbital-free DFT, World Scientific, Singapore (2012) (in press).

8 Motamarri, P., Iyer, M., Knap, J., Gavini, V., A numerical analysis of the finite-element discretization of orbital-free density functional theory, J. Comp. Phys. (submitted, 2011).

9 Motamarri, P., Nowak, M.R., Leiter, K., Knap, J., Gavini, V., A higher order adaptive finite-element discretization of Kohn-Sham density functional theory, (in preparation, 2012).

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